

5 ELECTROCHEMICAL CELL HAVING A PHYSICAL VAPOR  
DEPOSITED ELECTRODE AND METHOD OF MANUFACTURE

CROSS-REFERENCE TO RELATED APPLICATION

10 The present application is a divisional of  
application Serial No. 09/498,667, filed February 7,  
2000, which claims priority based on provisional  
application Serial No. 60/118,977, filed February 8,  
1999.

15 BACKGROUND OF THE INVENTION

1. Field Of The Invention

20 The present invention generally relates to the art  
of electrical energy storage devices and more  
particularly, to an electrode of an electrochemical cell  
or capacitor produced by a physical vapor deposition  
process.

25 2. Prior Art

Physical vapor plating involves introducing a  
material of interest into a vacuum and heating to a  
30 temperature at which the material reaches its vapor  
pressure. When molecular rays of the vaporized material  
attain a sufficient energy such that their mean free  
path causes them to impinge upon and precipitate onto a  
substrate, a coating of the material is formed. While  
35 physical vapor deposition processes are known in the

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5 art, as of yet, they have not been used to deposit an  
electrode active material onto a substrate to provide an  
electrode component for an electrochemical cell and to  
deposit a semiconductive or pseudocapacitive material  
10 onto a substrate to provide an electrode component for a  
capacitor.

## SUMMARY OF THE INVENTION

15 The present invention is directed to a novel and  
unique application of the physical vapor deposition  
process. The present process provides a coating of an  
electrochemically active material on a substrate,  
preferably a conductive substrate. The thusly produced  
coated substrate is useful as an electrode, for example,  
20 a cathode electrode incorporated into a primary  
electrochemical cell, and as the anode and/or the  
cathode of a secondary electrochemical cell. The  
assembly of the cell incorporating the electrode  
component made by physical vapor depositing an electrode  
25 active material onto a conductive substrate according to  
the present invention is preferably in the form of a  
wound element cell. That is, the fabricated cathode  
together with an anode and a separator are wound  
together in a "jellyroll" end type configuration or a  
30 "wound element cell stack" such that the anode is on the  
outside of the roll to make electrical contact with the  
cell case in a case-negative configuration. Other types  
of cells such as prismatic, bobbin shape and flat cells  
are also possible with the present invention.

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5 In the case of a capacitor, the present physical  
vapor deposition process is useful for producing an  
anode or a cathode in an electrochemical capacitor or  
the cathode in an electrolytic capacitor. Regardless  
the type, the capacitor configuration generally includes  
10 a substrate of a conductive metal such as titanium or  
tantalum provided with a semiconductive or a  
pseudocapacitive oxide coating, nitride coating, carbon  
nitride coating, or carbide coating.

15 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

One embodiment of the present invention is directed  
to the use of a physically vapor deposited coating of an  
electrode active material on a conductive substrate to  
20 thereby form an electrode component for an  
electrochemical cell. In one preferred embodiment, the  
electrode active material is a cathode active material  
deposited onto a substrate by means of a physical vapor  
deposition process to form a cathode component for an  
25 electrochemical cell. The cathode active material is  
selected from the group consisting of a metal, a metal  
oxide, mixed metal oxide, a metal sulfide and a  
carbonaceous material, and mixtures thereof. Suitable  
cathode materials include silver vanadium oxide, copper  
30 silver vanadium oxide, manganese dioxide, titanium  
disulfide, copper oxide, cobalt oxide, chromium oxide,  
copper sulfide, iron sulfide, iron disulfide, carbon and  
fluorinated carbon. The solid cathode exhibits

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5   excellent thermal stability and is generally safer and  
less reactive than a non-solid cathode.

Preferably, the solid cathode material comprises a  
mixed metal oxide formed by physical vapor depositing  
various metal oxides or metal oxide/elemental metal  
10   combinations. The materials thereby produced contain  
metals and oxides of Groups IB, IIB, IIIB, IVB, VB, VIB,  
VIIB and VIII of the Periodic Table of Elements, which  
includes the noble metals and/or their oxide compounds.

By way of illustration, and in no way intended to  
15   be limiting, an exemplary cathode active material  
comprises silver vanadium oxide having the general  
formula  $Ag_xV_2O_y$  in any one of its many phases, i.e.  
 $\beta$ -phase silver vanadium oxide having in the general  
formula  $x = 0.35$  and  $y = 5.18$ ,  $\gamma$ -phase silver vanadium  
20   oxide having in the general formula  $x = 0.74$  and  $y =$   
 $5.37$  and  $\epsilon$ -phase silver vanadium oxide having in the  
general formula  $x = 1.0$  and  $y = 5.5$ , and combination and  
mixtures of phases thereof. Preferably, the cathode  
active material, whether comprised of silver vanadium  
25   oxide or a similarly suitable material, is deposited  
onto a substrate of titanium, stainless steel, nickel,  
tantalum, platinum, gold or aluminum by a physical vapor  
deposition process. The thusly formed exemplary  
electrode can be incorporated into an alkali metal  
30   electrochemical cell, and more particularly, a lithium  
electrochemical cell.

Another preferred embodiment of the present  
invention comprises coating an alkalated material onto a  
conductive substrate of the above described materials by

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5 a physical vapor deposition process to provide a cathode  
for a secondary electrochemical cell. For example, in  
the case of the alkalated material being a lithiated  
material suitable materials include oxides, sulfides,  
selenides and tellurides of such metals as vanadium,  
10 titanium, chromium, copper, tin, molybdenum, niobium,  
iron, nickel, cobalt and manganese. Among the suitable  
oxides are  $\text{LiNiO}_2$ ,  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiCoO}_2$ ,  $\text{LiCo}_{0.92}\text{Sn}_{0.08}\text{O}_2$  and  
 $\text{LiCo}_{1-x}\text{Ni}_x\text{O}_2$ . The anode for such a secondary  
electrochemical cell can comprise a particulate  
15 carbonaceous composition including carbon together with  
a filamentary, electrically conductive material such as  
carbon black. Accordingly, it is further contemplated  
by the scope of the present invention that particulate  
carbonaceous compositions are physically vapor deposited  
20 onto a conductive substrate for use as an anode  
component in a secondary cell and as the cathode in a  
primary electrochemical cell.

Physical vapor deposited coatings rely mostly upon  
mechanical bonding to the substrate surface. It is,  
25 therefore, critical that the electrode substrate be  
properly prepared to ensure coating quality. It is  
especially necessary that the surface remain  
uncontaminated by lubricants from handling equipment or  
body oils from the hands. Suitable substrate surface  
30 preparation techniques include scraping, wire brushing,  
machining, grit blasting, or by chemical action. It  
also is recommended that the prepared surface be coated  
as soon as possible after preparation to prevent the  
possibility of contamination or surface oxidation.

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5       After substrate surface cleaning, surface roughness  
is the next most critical factor for properly applying a  
physical vapor deposited coating of electrode active  
material. Three methods of roughening the electrode  
10   rough threading, grit blasting, and a combination of  
rough threading, then grit blasting, as are well known  
to those skilled in the art of chemical vapor deposition  
techniques.

15       According to the present invention any one of the  
previously listed electrode active materials including  
the enumerated cathode active materials and the  
lithiated materials is heated in a vacuum to a  
temperature at which the material reaches its vapor  
pressure. A suitable vacuum pressure is about  $10^{-2}$  torr  
20   (about  $10^{-5}$  atm) or greater. Under such processing  
conditions, the vaporized material emits molecular rays  
in all directions. The vacuum must be great enough that  
the mean free path of the residual gas molecules is  
greater than the distance from the material evaporation  
25   source to the substrate being coated. Accordingly, the  
physical vapor deposition process of the present  
invention requires that the molecular vapor travel from  
its source to the substrate to form the desired coating  
without intermediate collision and precipitation.

30       One of the benefits of the present invention is  
that electrode plates made by a physical vapor  
deposition process according to the present invention  
are thinner than currently available electrodes. This  
provides for the manufacture of higher surface area

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5 cells housed in smaller containers than conventional  
electrode preparation technology permits. In that  
respect, the electrode active material can be coated on  
both sides of the substrate by a physical vapor  
deposition process to further increase the electrode  
10 active surface area. The substrate can also be  
perforated so that the coatings on both sides of the  
substrate are in physical contact with each other to  
lock the electrode active material onto the substrate.

The exemplary cell of the present invention having  
15 the cathode component made by the physical vapor  
deposition of a cathode active material onto a suitable  
substrate and preferably silver vanadium oxide deposited  
onto a titanium substrate, further comprises an anode  
selected from Group IA of the Periodic Table of  
20 Elements, including lithium, sodium, potassium, etc.,  
and their alloys and intermetallic compounds including,  
for example Li-Si, Li-B and Li-Si-B alloys and  
intermetallic compounds. The preferred anode comprises  
lithium.

25 The form of the anode may vary, but preferably the  
anode is a thin metal sheet or foil of the anode metal,  
pressed or rolled on a metallic anode current collector,  
i.e., preferably comprising nickel to form an anode  
component. In the electrochemical cell of the present  
30 invention, the anode component has an extended tab or  
lead of the same material as the anode current  
collector, i.e., preferably nickel integrally formed  
therewith such as by welding and contacted by a weld to  
a cell case of conductive metal in a case-negative

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5    electrical configuration. Alternatively, the anode may  
be formed in some other geometry, such as a bobbin  
shape, cylinder or pellet to allow an alternate low  
surface area cell design.

10    The exemplary cell of the present invention having  
the cathode component made by physical vapor depositing  
a cathode active material onto a suitable substrate  
includes a separator to provide physical separation  
between the anode and cathode active electrodes. The  
separator is of electrically insulative material to  
15    prevent an internal electrical short circuit between the  
electrodes, and the separator material also is  
chemically unreactive with the anode and cathode active  
materials and both chemically unreactive with and  
insoluble in the electrolyte. In addition, the  
20    separator material has a degree of porosity sufficient  
to allow flow therethrough of the electrolyte during the  
electrochemical reaction of the cell. Illustrative  
separator materials include non-woven glass,  
polypropylene, polyethylene, glass fiber material,  
25    ceramics, a polytetrafluorethylene membrane commercially  
available under the designations ZITEX (Chemplast Inc.),  
a polypropylene membrane commercially available under  
the designation CELGARD (Celanese Plastic Company Inc.)  
and DEXIGLAS (C.H. Dexter, Div., Dexter Corp.). Other  
30    separator materials that are useful with the present  
invention include woven fabric separators comprising  
halogenated polymeric fibers, for example of the type  
described in U.S. Patent No. 5,415,959 to Pyszczyk et  
al., which is assigned to the assignee of the present



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5 invention and incorporated herein be reference. Other  
suitable halogenated polymeric materials include, but  
are not limited to, polyethylene tetrafluoroethylene  
which is commercially available under the name Tefzel, a  
trademark of the DuPont Company;  
10 polyethylenechlorotrifluoroethylene which is  
commercially available under the name Halar, a trademark  
of the Allied Chemical Company and polyvinylidene  
fluoride.

The form of the separator typically is a sheet  
15 which is placed between the anode and cathode electrodes  
and in a manner preventing physical contact  
therebetween. Such is the case when the anode is folded  
in a serpentine-like structure with a plurality of  
cathode plates disposed intermediate the anode folds and  
20 received in a cell casing or when the electrode  
combination is rolled or otherwise formed into a  
cylindrical "jellyroll" configuration.

The exemplary electrochemical cell of the present  
invention having the cathode component made by physical  
25 vapor depositing a cathode active material onto a  
suitable substrate further includes a nonaqueous,  
ionically conductive electrolyte activating the anode  
and the cathode electrodes. The electrolyte serves as a  
medium for migration of ions between the anode and the  
30 cathode during the electrochemical reactions of the  
cell. The electrochemical reactions at the electrodes  
involves conversion of the migrating ions into atomic or  
molecular forms. Thus, nonaqueous electrolytes suitable  
for the present invention are substantially inert to the

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5 anode and cathode materials, and they exhibit those physical properties necessary for ionic transport, namely, low viscosity, low surface tension and wettability.

10 A suitable electrolyte has an inorganic, ionically conductive salt dissolved in a nonaqueous solvent, and more preferably, the electrolyte includes an ionizable alkali metal salt dissolved in a mixture of aprotic organic solvents comprising a low viscosity solvent and a high permittivity solvent. The ionically conductive  
15 salt serves as the vehicle for migration of the anode ions to intercalate or react with the cathode active material. In a solid cathode/electrolyte system, the preferred ion-forming alkali metal salt is similar to the alkali metal comprising the anode. Examples of  
20 salts useful with the present invention include  $\text{LiPF}_6$ ,  $\text{LiAsF}_6$ ,  $\text{LiSbF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiAlCl}_4$ ,  $\text{LiNO}_3$ ,  $\text{LiGaCl}_4$ ,  $\text{LiSO}_3\text{F}$ ,  $\text{LiB}(\text{C}_6\text{H}_5)_4$ ,  $\text{LiClO}_4$ ,  $\text{LiC}(\text{SO}_2\text{CF}_3)_3$ ,  $\text{LiSCN}$ ,  $\text{LiO}_3\text{SCF}_2\text{CF}_3$ ,  $\text{LiO}_2$ ,  $\text{LiC}_6\text{F}_5\text{SO}_3$ ,  $\text{LiO}_2\text{CCF}_3$ ,  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$  and  $\text{LiCF}_3\text{SO}_3$ , and mixtures thereof.

25 Low viscosity solvents include tetrahydrofuran (THF), methyl acetate (MA), diglyme, triglyme, tetraglyme, dimethyl carbonate (DMC), 1,2-dimethoxyethane (DME), diethyl carbonate, diisopropylether, 1,2-diethoxyethane (DEE), 1-ethoxy,2-  
30 methoxyethane (EME), dipropyl carbonate (DPC), ethylmethyl carbonate (EMC), methylpropyl carbonate (MPC) and ethylpropyl carbonate (EPC), and mixtures thereof, and high permittivity solvents include cyclic carbonates, cyclic esters and cyclic amides such as

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5 propylene carbonate (PC), butylene carbonate (BC),  
ethylene carbonate (EC), acetonitrile, dimethyl  
sulfoxide, dimethyl formamide, dimethyl acetamide,  
γ-valerolactone, γ-butyrolactone (GBL) and N-methyl-  
pyrrolidinone (NMP) and mixtures thereof. In the  
10 preferred electrochemical cell comprising the Li/SVO or  
the Li/CSVO couple, the preferred electrolyte is 1.0M to  
1.4M  $\text{LiPF}_6$  or  $\text{LiAsF}_6$  in a 50:50 mixture, by volume, of PC  
and DME.

One preferred form of the cell assembly described  
15 herein is referred to as a wound element cell. That is,  
the fabricated cathode, anode and separator are wound  
together in a "jellyroll" end type configuration or  
"wound element cell stack" such that the anode is on the  
outside of the roll to make electrical contact with the  
20 cell case in a case negative configuration. Using  
suitable top and bottom insulators, the wound cell stack  
is inserted into a metallic case of a suitable size  
dimension. The metallic case may comprise materials  
such as stainless steel, mild steel, nickel-plated mild  
25 steel, titanium or aluminum, but not limited thereto, so  
long as the metallic material is compatible for use with  
components of the cell.

The cell header comprises a metallic disc-shaped  
body with a first hole to accommodate a glass-to-metal  
30 seal/terminal pin feedthrough and a hole for electrolyte  
filling. The glass used is of a corrosion resistant  
type having from between about 0% to about 50% by weight  
silicon such as CABAL 12, TA 23 or FUSITE 425 or FUSITE  
435. The positive terminal pin feedthrough preferably

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5 comprises titanium although molybdenum and aluminum can  
also be used. The cell header comprises elements having  
compatibility with the other components of the  
electrochemical cell and is resistant to corrosion. The  
cathode lead is welded to the positive terminal pin in  
10 the glass-to-metal seal and the header is welded to the  
case containing the electrode stack. The cell is  
thereafter filled with the electrolyte described  
hereinabove and hermetically sealed such as by  
close-welding a stainless steel ball over the fill hole,  
15 but not limited thereto. This above assembly describes  
a case negative cell which is the preferred construction  
of the exemplary cell of the present invention. As is  
well known to those skilled in the art, the exemplary  
electrochemical system of the present invention can also  
20 be constructed in a case positive configuration.

Another embodiment of the present invention is  
directed to the use of a physically vapor deposited  
coating of a semiconductive or pseudocapacitive oxide  
coating, nitride coating, carbon nitride coating, or  
25 carbide coating. The coating is deposited on a  
substrate of a conductive metal such as titanium,  
molybdenum, tantalum, niobium, cobalt, nickel, stainless  
steel, tungsten, platinum, palladium, gold, silver,  
copper, chromium, vanadium, aluminum, zirconium,  
30 hafnium, zinc and iron, and mixtures and alloys thereof.  
The semiconductive or pseudocapacitive material includes  
an oxide of a first metal, or a precursor thereof, the  
nitride of the first metal, or a precursor thereof, the  
carbon nitride of the first metal, or a precursor

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5 thereof, and/or the carbide of the first metal, or a  
precursor thereof, the oxide, nitride, carbon nitride  
and carbide of the first metal having pseudocapacitive  
properties. The first metal is preferably selected from  
the group consisting of ruthenium, cobalt, manganese,  
10 molybdenum, tungsten, tantalum, iron, niobium, iridium,  
titanium, zirconium, hafnium, rhodium, vanadium, osmium,  
palladium, platinum, and nickel.

The porous coating may also include a second or  
more metals. The second metal is in the form of an  
15 oxide, a nitride, a carbon nitride or a carbide, or  
precursors thereof and is not essential to the intended  
use of the coated foil as a capacitor electrode and the  
like. The second metal is different than the first  
metal and is selected from one or more of the group  
20 consisting of tantalum, titanium, nickel, iridium,  
platinum, palladium, gold, silver, cobalt, molybdenum,  
ruthenium, manganese, tungsten, iron, zirconium,  
hafnium, rhodium, vanadium, osmium, and niobium. In a  
preferred embodiment of the invention, the porous  
25 coating includes oxides or ruthenium and tantalum, or  
precursors thereof.

The thusly fabricated semiconductive or  
pseudocapacitive coated substrates are useful as an  
anode or a cathode in an electrochemical capacitor or  
30 the cathode in an electrolytic capacitor. For  
additional disclosure directed to such capacitors,  
reference is made to U.S. Patent No. 5,926,362 to  
Muffoletto et al., which is assigned to the assignee of  
the present invention and incorporated herein by

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5 reference. For a more thorough understanding of the  
chemical vapor deposition process, reference is made to  
the book Vapor Deposition, edited by Carroll F. Powell,  
Joseph H. Oxley and John M. Blocker, Jr. of the Battelle  
Memorial Institute, Columbus, Ohio, published by John  
10 Wiley & Sons, Inc., the disclosure of which is  
incorporated herein by reference.

It is appreciated that various modifications to the  
invention concepts described herein may be apparent to  
those skilled in the art without departing from the  
15 spirit and the scope of the present invention defined by  
the hereinafter appended claims.

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